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Siloxanes containing at least one Si-H bond undergo a redistribution reaction catalyzed by transition metal complexes of Ir, Rh, and Pt. A new metalla-cyclodisiloxane of Ir is described.

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Redistribution Reactions of Methylsiloxanes

Catalyzed by Transition Metal Complexes

by

W.A. Gustavson, P.S. Epstein, and M.D. Curtis

Prepared for publication in the

Journal of Organometallic Chemistry

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REDISTRIBUTION REACTIONS OF METHYLSILOXANES CATALYZED BY TRANSITION METAL COMPLEXES.[1]
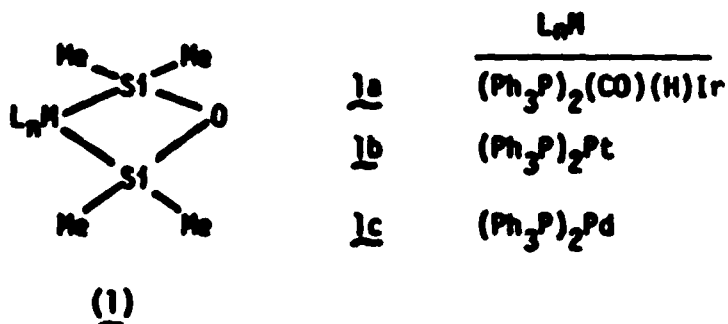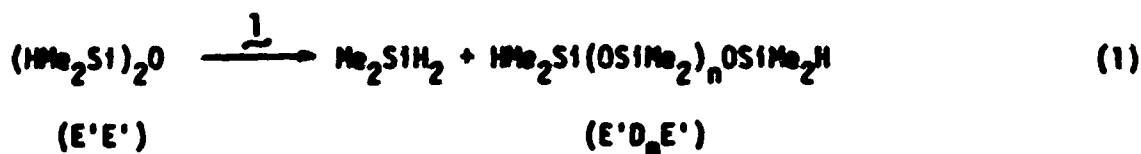
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ABSTRACT

Redistribution reactions of a variety of hydrogen-substituted siloxanes
are catalyzed by various transition metal complexes of iridium and
rhodium. The products arise from breaking and remaking of Si-C, Si-H,
and Si-O bonds. Siloxanes not possessing a Si-H bond are inert under
the conditions studied. The most favored reaction pathway appears to
preferentially scramble the groups directly attached to the silicon bear-
ing the hydrogen atom. A new cyclo-iridiadisiloxane, $L_2(CO)(H)$ —
$\overline{Ir(SiMeROSiMeR)}$ (L = Ph_3P, R = Me_3SiO) is reported. This compound exists
in three isomeric forms as a consequence of the spatial arrangements
of the R and Me groups on the ring.

I.

INTRODUCTION

In an investigation of small-ring metallacycles, Curtis and Greene[1] found that cyclo-metalladisiloxanes, 1, were catalysts for the disproportionation of tetramethyldisiloxane $(E'E')^2$ into dimethylsilane and oligomeric siloxanes $(E'D_nE')^2$ (eq. 1).

$$(HMe_2Si)_2O \xrightarrow{\ 1\ } Me_2SiH_2 + HMe_2Si(OSiMe_2)_nOSiMe_2H \qquad (1)$$

$$(E'E') \qquad\qquad\qquad (E'D_nE')$$

		L_nM
1a		$(Ph_3P)_2(CO)(H)Ir$
1b		$(Ph_3P)_2Pt$
1c		$(Ph_3P)_2Pd$

(1)

A mechanism was proposed[1b,c] in which the strain in the four membered ring assisted the scission of an Si-O bond in 1 to give reactive, coordinated silylene and silanone intermediates. The crystal structure of 1a lent support to the argument that the Si-O bond is weakened in the metallacycle.[3]

The proposed mechanism dealt specifically with the iridium complex, 1a, but could be extended to some of the other complexes with minor modifications. Some consequences of the proposed mechanism are that: (1) only those siloxanes possessing the 1,3-dihydrido functionality would undergo facile redistribution

since only the Si-H bond reacts readily with the low valent metal complexes, and the 1,3-arrangement is necessary to form the four-membered ring; (2) only SiO/H exchange (see below) should occur, and (3) the oligomers are formed sequentially, i.e., $2E'E' \rightarrow E'DE' + Me_2SiH_2$; $E'E' + E'DE' \rightarrow E'D_2E' + Me_2SiH_2$; $E'E' + E'D_2E' \rightarrow E'D_3E' + Me_2SiH_2$, etc.

The general features of the Ir-catalyzed reaction seemed to fit all these requirements, at least at low conversions.[1c] After longer reaction times, various secondary products were observed. In order to further characterize the redistribution reaction and the effects of using different metals and different silanes, the present work was undertaken. The results show that the reaction is much more complex than originally thought and that the originally proposed metallacycle mechanism, if it is operative at all, cannot be the only mechanism whereby the groups on silicon are redistributed.

EXPERIMENTAL

All manipulations involving solutions of catalysts, reaction mixtures, etc. were done with standard Schlenk techniques under a nitrogen atmosphere. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded on a Jeol JNM-PS-100 spectrometer or on a Varian T-60A. Gas chromatograms were obtained on an Antek 300, dual column instrument equipped with a thermal conductivity detector. Recording and integration of the GC spectra were accomplished with a Hewlett Packard 3380A integrator-plotter. The analytical column employed was 14' x 1/8" S.S. packed with 5% SE-30 on Chromosorb WHP 80/100. The carrier gas was He at a flow rate of 10 mL/min. Typical GC conditions are: Injector, 250°; Detector, 300°; temperature program: 2 min. at 40°, then increase at 4°/min. to 225°. The preparative GC column consisted of 15' x 1/4" S.S. packed with 20% SE-30 on

chromosorb A 40/60.

Mass spectra were recorded on an AEI MS902 (pure components) or on the Finnegan 4000 quadrupole spectrometer interfaced to a temperature programmable GC column, the whole being controlled by the INCOS data acquisition system.[4] When operating in the GC/MS mode, the spectra were typically "enhanced", a procedure whereby the computer substracts out peaks which are judged to be background on the basis of their mass chromatograms. Parent ions were located either by mass chromatography (mass vs. time) or by chemical ionization techniques.[4]

In cases where mass spectrometry alone would not resolve the identity of a compound, e.g., between the isomers E'DDE' and ED'D'E, the substance in question was isolated by preparative GC and analyzed by ^{1}H- and/or ^{13}C-NMR spectroscopy. Once the identity of a compound was established, its mass spectrum was stored in the computer library. Future occurances of the compound in mixtures could then be established by comparing its mass spectrum with the library spectrum peak for peak.

The following code will be used in the Tables to indicate the manner in which various substances were identified: 1 - Comparison of GC retention times and computer matching of the mass spectra to those of authentic samples, 2 - as in method 1 plus the isolation of the product by preparative GC and analysis of its ^{1}H- and/or ^{13}C-NMR spectra, 3 - analysis based on comparing GC retention times and MS fragmentation patterns with similar substances according to empirical rules developed in the course of this work[5] and by others[6], 4 - as in methods 1 or 3 plus substitution of Ph by Ph-d_5.

Starting siloxanes were purchased from Petrarch and were distilled prior to use. Tetramethyldisiloxane was prepared by hydrolysis of Me$_2$SiHCl, obtained from Dow Corning Corp. Vaska's and Wilkinson's complexes, L$_2$(CO)ClIr and L$_3$RhCl, respectively, were prepared by literature methods.[7,8] Benzene

was dried over potassium/benzophenone and distilled under N_2 immediately prior to use.

Synthesis of Hydrido -1,3-[trans-bis(1,3-trimethylsiloxy)-1,3-dimethyldisiloxanediyl]carbonylbis(triphenylphosphine)iridium(III), $L_2(CO)(H)Ir[SiMe(OSiMe_3)OSiMe(OSiMe_3)]$. 3.

Vaska's complex, $L_2(CO)ClIr$ (0.6g, 0.8 mmole) was slurried in 10 ml of benzene. Then, 0.45 g (1.5 mmole) of 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (ED'O'E) was added to give a cloudy, yellow solution which became clear when heated to reflux. After stirring at reflux for 1 hr., the solvent was removed under vacuum to give an oil. Trituration with benzene/pet. ether gave a white solid, m.p. 158-160°, in 78% yield based on Ir. The 60 MHz ^{1}H-NMR of 2 in the SiMe region consists of two broad peaks at δ0.8 and 0.6 and a sharper peak at δ0.2. Each of these peaks is obviously composed of overlapping unresolved peaks.

Anal.: Calcd. for $C_{46}H_{56}IrP_2O_4Si_4$: C,52.65; H,5.42; P,6.03; Si, 10.95; Ir, 18.72. Found: C, 52.04; H, 5.48; P, 6.10; Si, 10.20; Ir, 17.70. The SiOSi stretch occurs as a v. strong band between 1000 - 1100 cm^{-1}. ν_{IrH}:2080(s); ν_{CO}: 1967(s) cm^{-1}.

Redistribution Reactions.

The conditions for each run are listed as footnotes in the Tables. A typical procedure is described here. Tetramethyldisiloxane (7.5 ml, 42 mmole) was added to a benzene solution (25 ml) containing 200 mg (0.26 mmole) of $(Ph_3P)_2(CO)ClIr$ under a N_2-atmosphere. The reaction flask was equipped with a reflux condenser, N_2 inlet, and an oil bubbler (attached at the top of the condenser and connected to the N_2 source through a T-joint). During the reaction, a static N_2 blanket was maintained in the reaction vessel. The flask was immersed in a constant temperature

bath for a given time. The bulk of the solvent was then
distilled off and the solvent fraction and pot residue analyzed by GC or
GC/MS. This concentration step allowed for better determination of minor
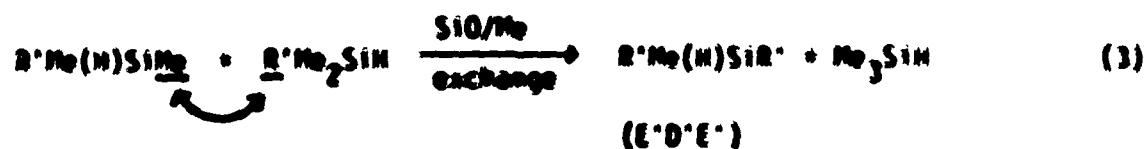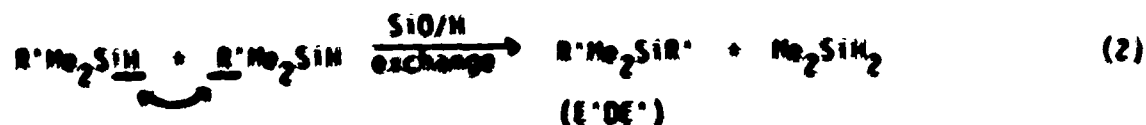components.

Kinetic Runs. In those cases where the kinetics of the redistribution
reactions were determined, the reaction flask was also fitted with a 4 mm
diameter side-arm tipped with a septum for GC sampling during the course of
the reaction. In addition, a weighed amount of internal standard (n-heptane
or n-octane) was added to the stock solutions of catalyst.

RESULTS AND DISCUSSION

Tables I-IV list some of the products observed when various siloxanes
containing an Si-H bond are treated with transition metal
complexes. In addition to the complexes listed, several others, e.g.,
$Rh_2(CO)_4Cl_2$, $Rh_2(C_2H_4)_4Cl_2$, $(C_2H_4)_2Rh(acac)$, and $L_2\overline{Pt(SiMe_2OSiMe_2)}$ (L =
Ph_3P unless explicitly stated otherwise), also were found to catalyze the re-
distribution of tetramethyldisiloxane, E'E'. However, the products are essentially
the same as those listed in Table I.

Siloxanes which do not have at least one Si-H bond are inert under the
conditions described in Tables I-IV. Thus, D_3, D_4, EE, and EDE remain unchanged
in the presence of the transition metal complexes which cause redistribution
of hydrido-siloxanes. These permethylsiloxanes are also inert in the presence
of a hydrido silane and the transition metal complex. This latter observation
rules out the possibility that the observed reactions occur as a result of
catalysis by acidic metal "hydrides" formed in the reaction mixture.

As Table 1 shows, all the redistribution products of E'E' may be rationalized as arising from exchanges of groups adjacent to the Si-H functionality (e.g., eqs. 2,3; R' = HMeSiO-).
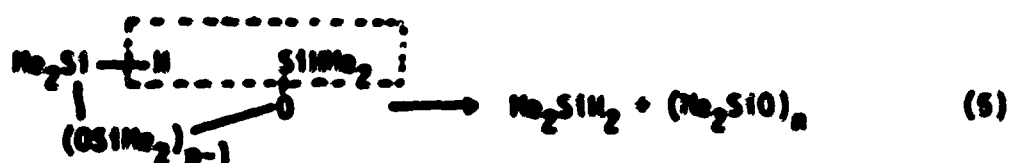
$$R'Me_2SiH + \underline{R'Me_2SiH} \xrightarrow{\text{SiO/H exchange}} R'Me_2SiR' + Me_2SiH_2 \qquad (2)$$
$$(E'DE')$$

$$R'Me(H)SiH + \underline{R'Me_2SiH} \xrightarrow{\text{SiO/Me exchange}} R'Me(H)SiR' + Me_3SiH \qquad (3)$$
$$(E'D'E')$$

A second SiO/H exchange on E'DE' with E'E' (present in excess) gives the next higher oligomer according to eq. 4 (R" = Me$_2$SiOSi(Me)$_2$O-). Continuing

$$R"SiMe_2H + \underline{R'Me_2SiH} + R"SiMe_2R' + Me_2SiH_2 \qquad (4)$$
$$(E'DE') \qquad\qquad (E'D_2E')$$
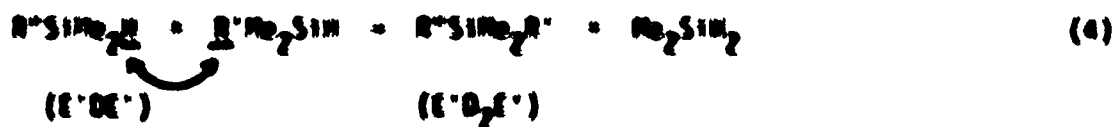
in this manner, the oligomers E'D$_n$E' are formed sequentially via SiO/H exchange. This is by far the most favored reaction pathway for the iridium catalysis of E'E' redistribution, and is the reaction pathway in accord with the metalla-cycle mechanism previously proposed.[1b,c]

However, the minor products appear to arise from SiO/Me exchange as shown in eq. 3. Other minor products, e.g., the cyclic oligomers D_3 and D_4, can be accounted for on the basis of an internal SiO/H exchange as shown in eq. 5 (i.e., $E'D_{n-1}E' \rightarrow Me_2SiH_2 + D_n$).

$$Me_2Si \underset{\underset{(OSiMe_2)_{n-1}}{|}}{\overset{|}{\longrightarrow}} \begin{array}{c} SiMe_2 \\ | \\ 0 \end{array} \longrightarrow Me_2SiH_2 + (Me_2SiO)_n \qquad (5)$$

Neither SiO/Me exchange nor the internal SiO/H exchange of eq. 5 can be accommodated easily by the metallacycle mechanism. Although there could be two or more mechanisms operative, a faster one involving metallacycles which give the main products and slower ones accounting for the various minor products, it seems more likely that the metallacycles are not directly involved in the catalytic cycle.

With the Ir-catalyzed reactions shown in Table I, SiO/H exchange accounts for 88% of the products shown. Only 50% of the products from the Rh-catalyzed reaction (Table I) can be attributed to SiO/H exchange. The Rh-catalyzed reaction also does not give the product distribution predicted on the basis of sequential oligomer formation, $E'DE' \rightarrow E'D_2E' \rightarrow E'D_3E'$, etc. As Figure 1 shows, the oligomer $E'D_2E'$ is in greater concentration than $E'DE'$ at all times.

The metallacycle mechanism predicts the initial concentration of $E'DE'$ to be higher than that of $E'D_2E'$ since $E'DE'$ is the initial, "1st turnover" product. Hence, some other mechanism must be operative, even for SiO/H exchange, with the rhodium-based catalysts. (Note: oxygen balance requires three moles of $E'E'$ to produce one of $E'D_2E'$ no matter what the mechanism.)

The siloxanes, pentamethyldisiloxane (EE') and hexamethyltrisiloxane ($E'DE'$), were subjected to redistribution conditions with $L_2(CO)ClIr$ as catalyst. EE' does not have the second hydrogen necessary to form a four-membered metallacycle and $E'DE'$ has been shown to give the six-membered metallacycle, 2.[1c]

$$L_2(CO)ClIr + E'DE' \rightarrow \qquad (6)$$

$$(2)$$
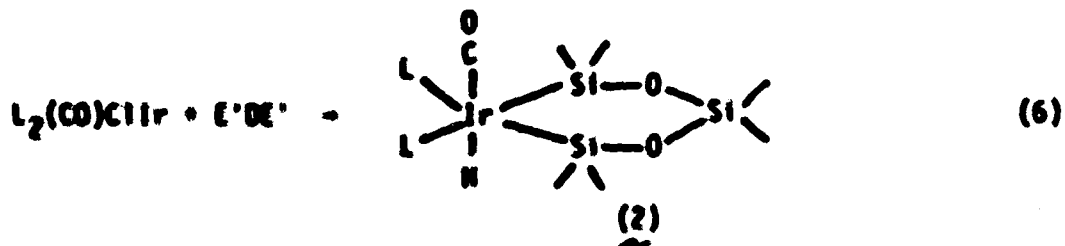
These siloxanes undergo redistribution, although at a rate slower than that for $E'E'$. Figure 2 shows a graph of concentration vs. time for the redistribution of EE' and $E'E'$. These curves are typical for all the redistribution reactions studied to date. There is an initial rapid drop in siloxane concentration, then an abrupt break followed by a slow, zero-order reaction. The zero-order rate constants from the data in Figure 2 are 6×10^{-5} and 85×10^{-5} mmole/ml/min for EE' and $E'E'$, respectively. Dividing by the concentration of catalyst gives the turnover numbers, 1.1×10^{-3} and 1.6×10^{-2} moles siloxane/mole
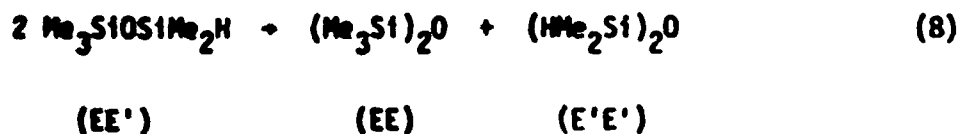
catalyst/min., for EE' and E'E', respectively. The rate for E'E' is thus about 16 times that for EE'. Whether or not the relatively modest rate increase for E'E' is due to the operation of the special, metallacyclic mechanism is questionable.

It was also observed that the following catalyst precursors all gave the same turnover numbers after the initial abrupt drop: L_3RhCl, $(acac)Rh(ethylene)_2$ and $Rh_2(CO)_4Cl_2$. This suggests that the final catalytic species are identical.

The redistribution products of pentamethyldisiloxane (EE') are shown in Table II. The major product is ED'E which most likely comes from an exchange of trimethylsiloxy for methyl on EE' (eq. 7). The unsymmetric

$$2 \ Me_3SiOSiMe_2H \ \rightarrow \ Me_3SiOSiMe(H)OSiMe_3 + Me_3SiH \qquad (7)$$

$$\text{(EE')} \qquad\qquad \text{(ED'E)}$$
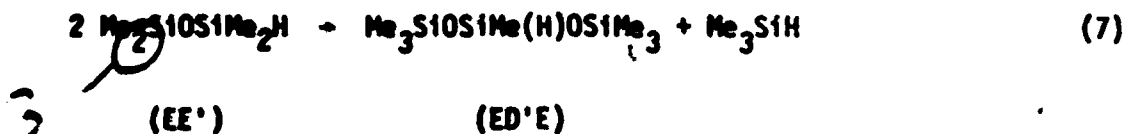
nature of EE' also reveals that SiO/SiO exchanges must occur, e.g., eq. 8.

$$2 \ Me_3SiOSiMe_2H \ \rightarrow \ (Me_3Si)_2O \ + \ (HMe_2Si)_2O \qquad (8)$$

$$\text{(EE')} \qquad\qquad \text{(EE)} \qquad\qquad \text{(E'E')}$$

The E'E' disproportionates further. In fact, all of the "symmetric" oligomers, $E'D_nE'$ in Table II most probably result from SiO/SiO exchanges.

Table III presents the redistribution products of E'DE'. One of the major products, E'D$_2$E', is again most probably formed as a result of the SiO/SiO exchange shown in the Table. The other major product is the cyclic tetramer, D$_3$D'. If this cyclic forms from an internal exchange (cf. eq. 5), then its precursor is E'DD'DE', the expected first turnover product resulting from the SiO/Me exchange shown in the Table. If this scheme is correct, then the E'DD'DE' must cyclize nearly as fast as it is formed since its concentration is extremely low for a 1st turnover product.

ED'D'E reacts with L$_2$(CO)ClIr to give a mixture of the metallacycles 3a-3c (R = Me$_3$SiO).[9] The overall composition is well established by elemental
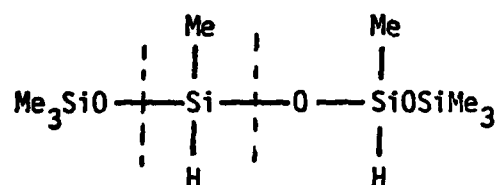

(3a)   (3b)   (3c)
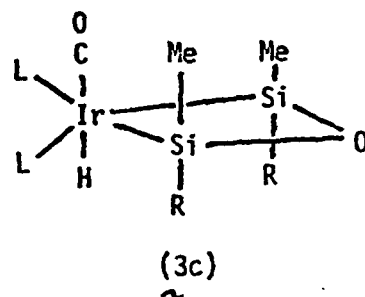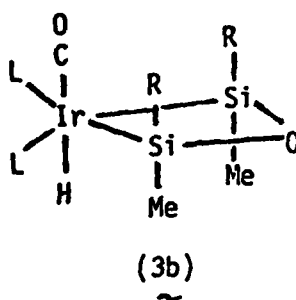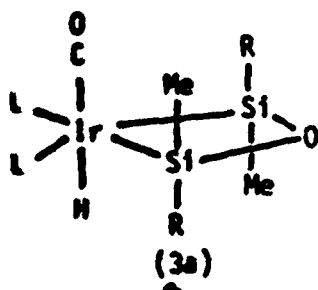
analysis. However, the ^{1}H-NMR in the Si-Me region consists of a set of overlapping peaks in three main "bunches" at δ 0.8, 0.6 and 0.2. Five peaks and two shoulders are distinguishable. The mixture of isomers 3-5 should give a total of eight methyl environments.

If the redistribution reaction of ED'D'E were to proceed via the previously proposed metallacycle mechanism, then the primary reaction products would be given by eq. 9 (R = Me_3SiO). The oligomeric siloxanes should

$$(n+1)ED'D'E \rightarrow ED'(-\underset{\underset{E}{|}}{T}-)_n D'E + n\ RMeSiH_2 \qquad (9)$$
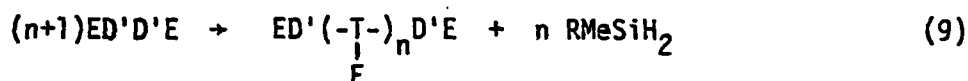
have pendant Me_3SiO groups along the polymer backbone. The $RMeSiH_2$ should disproportionate very rapidly to give products, e.g., $MeSiH_{3(g)}$ and ED'E via R/H (R = Me_3SiO) exchanges.[9] However, the products listed in Table IV are best rationalized by assuming that both SiO bonds adjacent to the hydrogen-bearing silicon are labilized, not just the central Si–O bond as would be the case if a metallacycle were necessary to cause labilization.

$$Me_3SiO \overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle H}{|}}{Si}} - O - \overset{\overset{\displaystyle Me}{|}}{\underset{\underset{\displaystyle H}{|}}{Si}}OSiMe_3$$

In other words, ED'_2E, upon its interaction with the catalyst, supplies E, ED'_2, and ED' groups for exchange with SiO, Si-Me, and Si-H bonds. The predicted "1st turnover" products are then given by the following equations:

SiO/SiO exchanges:

$$ED_2^!E \rightarrow [E, D_2^!E, ED'] \rightarrow ED'E + ED_3^!E + ED_4^!E \qquad (10)$$
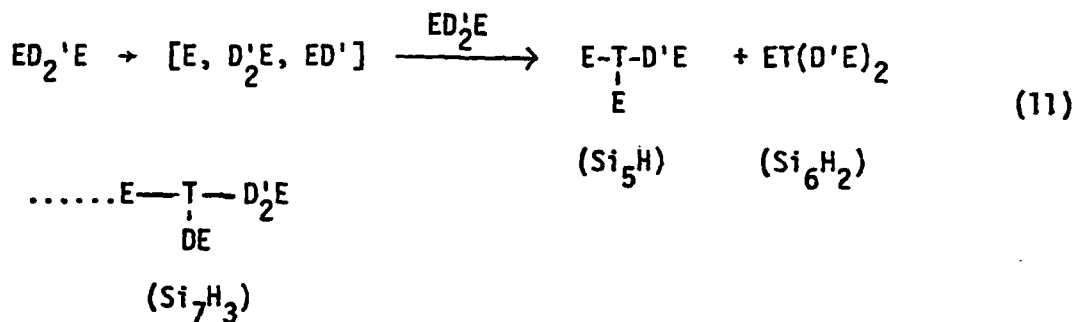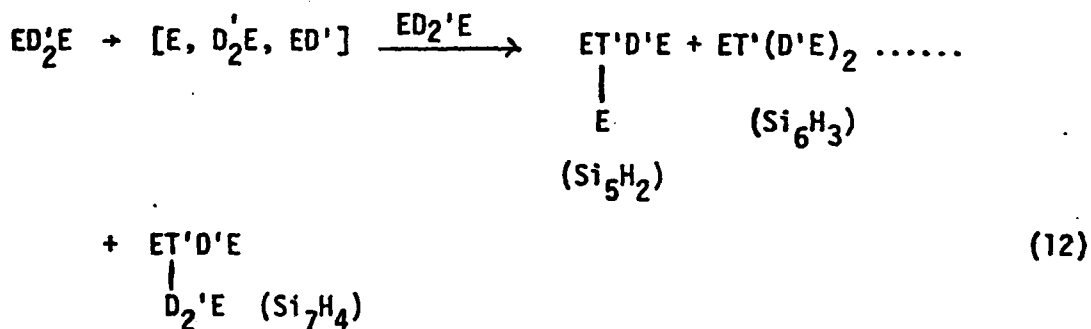
SiO/H exchanges:

$$ED_2'E \rightarrow [E, D_2^!E, ED'] \xrightarrow{ED_2^!E} \begin{array}{c} E\text{-}T\text{-}D'E \\ | \\ E \end{array} + ET(D'E)_2 \qquad (11)$$

$$ (Si_5H) \qquad (Si_6H_2)$$

$$\dots\dots E\!-\!\!\begin{array}{c}T\\|\\DE\end{array}\!\!-\!D_2^!E$$

$$(Si_7H_3)$$

SiO/Me exchanges:

$$ED_2^!E \rightarrow [E, D_2'E, ED'] \xrightarrow{ED_2'E} \begin{array}{c} ET'D'E \\ | \\ E \end{array} + ET^{\cdot}(D'E)_2 \dots\dots$$

$$ (Si_5H_2) (Si_6H_3)$$

$$+ \begin{array}{c} ET'D'E \\ | \\ D_2'E \end{array} (Si_7H_4) \qquad (12)$$
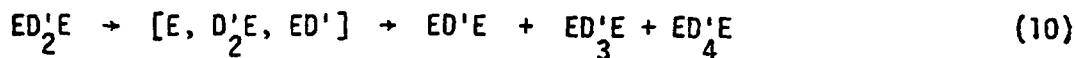
Of the predicted possibilities, ED'E is definitely observed; and Si_5H, Si_5H_2, two Si_6H_2 isomers, and an Si_7H_3 isomer are observed. These may possibly correspond to the underlined species in eq. 10-12. The remaining species can all be rationalized as "2nd turnover" products resulting from E/H, ED'/H, $ED_2^!/H$, etc. exchanges on the "1st turnover" products. It is interesting to note

that the Si_8H_2 isomer of possible structure, $ED'[T(E)]_2D'E$, is a "2nd turnover" product according to this scheme, but has the second highest concentration of any product. This same phenomenon occurs in the Rh-catalyzed redistribution of $E'E'$ wherein the "2nd turnover" product, $E'D_2E'$ has a higher concentration than the supposed "1st turnover" product, $E'DE'$ (see Fig. 1). In any event, the metal complex catalyzed redistribution of $ED_2'E$ leads to a very complex mixture, the composition of which is consistent with the notion that SiO and SiMe bonds adjacent to Si-H bonds are labilized and undergo exchange reactions.

Finally, we note that the metal species which are formed in the presence of Si-H bonds are sufficiently active to activate the C-H bond of benzene to substitution by Si.[10] As shown in Tables I and II, various phenyl substituted siloxanes and silanes are produced along with the rearrangement products. That the benzene solvent is the source of these phenyl groups in the case of iridium catalysts was demonstrated by using C_6D_6 as the solvent. The resulting phenyl-containing products are d_5-substituted and their fragmentation patterns are entirely consistent with their being d_5-phenyl groups.[5]

SUMMARY

Siloxanes having at least one Si-H bond undergo redistribution reactions in the presence of certain transition metal complexes, especially those of Pt, Pd, Ir and Rh. The observed products are formed as a result of scrambling all the groups attached to the silicon bearing the hydrogen atom; and, to a much lesser extent, as a result of more common SiO/SiO exchanges as observed

with acid or base catalyzed rearrangements.[1b,11] It appears that with the transition metal catalysts, SiO/Me and SiO/H exchanges are faster than SiO/SiO exchanges, so that these redistributions compliment the classical acid or base catalyzed redistributions. Synthetically useful rates and selectivities have been achieved recently by supporting the iridium complexes on high surface area oxides.[12]

The nature of the metal-silyl species involved in the catalytic cycle is unclear, although several possibilities have been discussed in some detail.[1b] Likely intermediates are mono- and dinuclear silylene complexes and complexed silanones. The remarkable stability of appropriately substituted silylenes has been demonstrated recently,[13] and silanones are commonly postulated as intermediates.[14]

ACKNOWLEDGEMENTS

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    Organosilanes". Other papers in this series: (a) Part III; W. A.
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    (b) Part II: M. D. Curtis and P. S. Epstein, Adv. Organometal. Chem. 19
    (1981) 213-255; (c) Part I: M. D. Curtis and J. Greene, J. Am. Chem. Soc.
    100 (1978) 6362.

2. The abbreviated notation for silicones used here is as follows:
    $\underline{E}$ (end group) = $Me_3SiO_{1/2}$, $\underline{D}$ (difunctional) = $Me_2SiO_{2/2}$; $\underline{T}$ (trifunctional) =
    $MeSiO_{3/2}$. A primed letter indicates a substitution of hydrogen for methyl
    (i.e., D' = $HMeSiO_{2/2}$), and a superscript "P" indicates substitution of
    phenyl for methyl (e.g., E^P = $PhMe_2SiO_{1/2}$-). For example:
    $Me_3SiOSiMe_2H$ = EE'; $PhMe_2SiOSiMe_2OSiMe_2H$ = E^P DE'; $(Me_3SiO)_3SiH$ = E_3T', etc.

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Table 1. Redistribution Products of tetramethyldisiloxane (E'H E') Catalyzed by $L_2(CO)ClIr$ and L_3RhCl

Product		$\Sigma(Ir)^a$	$\Sigma(Rh)^b$	Anal.	exchange type	substrate
Si₁	PhSiMe₂H	1.1	-	1	Ph/Hᵉ	Me₂SiH₂
Si₂	E'E'	1.0	2.0	1	Ph/Hᵉ	E'E'
Si₃	E'DE'	60.4	8.7	3	SiO/H	E'E'
	D₃	-	5	1	SiO/Hᶠ	E'D₂E'
	E'D'E'	0.5	0.8	1	SiO/Me	E'DE'
	D₂D'	0.4	0.8	3	SiO/Meᶠ	E'D₂E'
Si₄	E'D₂E'	21	13	2	SiO/H	E'DE'
	E'DD'E'	1.4	13	3	SiO/Me	E'DE'
	E'D₂E'		1.3	3	SiO/Me	E'DE'
	D₄	trace	4.1	1	SiO/Hᶠ	E'D₃E'
	D₃D'	1.1	-	3	SiO/Meᶠ	E'D₃E'
Si₅	E'D₃E'	2.0	8.6	1	SiO/H	E'D₂E'
	E'D₂D'E'	6.0	10.3	3	SiO/Me	E'D₂E'
	E'DD'DE'	0.2	4.0	3	SiO/Me	EDD'E'
Si₆	E'D₄E'	2.0	11.3	1	SiO/H	E'D₃E'

Table 1 (continued)

Footnotes

a) 4 mL E'E', 2 mL PhH, 120 mg $L_2(CO)ClIr$ (140:1 E'E': $L_2(CO)ClIr$), 60°, 48 hr. (39% conversion).

b) 6 mL E'E', 4 mL PhH, 120 mg L_3RhCl (280: 1 E'E':Rh) catalyst, 60°, 17 hr. (0% conversion).

c) Analysis code - see experimental section.

d) SiO/H refers to the reaction: $\underline{Si(Me)_2H}$ + E'E' → $Si(Me)OSiMe_2H$ + Me_2SiH_2; SiO/Me refers to:

$\underline{Si(Me)(H)}$ + E'E' → $Si(H)OSiMe_2H$ + Me_3SiH. The underlined species are considered to be the substrates.

e) Exchange with benzene solvent (see text).

f) Internal exchange (see text).

TABLE 11. Redistribution Products of Pentamethyldisilane (EE').[a]

Product		Area %[b]	Anal.[c]	Product		Area %[b]	Anal.[c]
Si$_2$	EE	3.8		Si$_6$	ED$_4$E	0.2	1
Si$_3$	EDE	4.8	2		ED$_4$E'	0.2	1
	ED'E	60.2	2		E'D$_4$E'	0.1	1
	EDE'	5.7	1				
Si$_4$	ED$_2$E	3.8	2	Si$_7$	ED$_5$E	0.1	2
	EDD'E	6.4	2		ED$_5$E'	0.1	3
	E'D$_2$E'	6.4	2		E'D$_5$E'	0.1	1
	E'DD'E'	1.7	3				
Si$_5$	ED$_3$E	0.7	1	Phenylsilanes[d]			
	ED$_2$D'E	0.9	3		E''E	2.1	4
	ED$_3$E'	0.6	1		E''DE	1.5	4
	E'D$_3$E'	0.1	1		E''D$_2$E	0.8	4

a) 39 mmole EE' and 0.773 mmole L$_2$(CO)Cl Ir in 15.0 ml C$_6$D$_6$ for 116 hr. at 70°, 18% conversion.

b) GC area percents of products with 2N silicon per molecule. Some Me$_3$SiH and EE also detected.

c) Analysis code - see experimental section.

d) Phenyl groups from solvent - see text.

TABLE III. Redistribution Products of Hexamethyltrisiloxane (E'DE').

Products[a]	Area %[b]	Formation[c]
Me₃SiH	0.1	—
E'DD'E	0.8	E'/Me on E'DE'
D₃D'	48.3	Cyclization of E'DD'DE' (?)
E'D₂E'	38.1	E'D/E' on E'DE'
E'DD'DE'[d]	1.0	E'D/Me on E'DE'
E'D₃E'	6.1	E'D/H on E'DE'
E'D₄E'	5.3	E'D/H on E'D₂E'

a) 2.04 M E'DE' in benzene; .01 M L₂(CO)ClIr, 80°, 46 hr. (6% conversion).

b) GC area percents of products only.

c) Probable mode of formation.

d) Structure assigned on basis of expected exchange mode.

TABLE IV. Redistribution Products of Octamethyltetrasiloxane, ED'O'E

Product[a,b]	Area %[c]	empirical formula
ED'E	13.9	$Me_7Si_3HO_2$
E_3T	3.4	$Me_{10}Si_4O_3$
$E_2T'D'E$	1.9	$Me_{10}Si_5H_2O_4$
$E_2TD'E$	7.5	$Me_{11}Si_5HO_4$
$ET(D'E)_2$	6.0	$Me_{12}Si_6H_2O_5$
$E_2TD'_2E$	1.0	$Me_{12}Si_6H_2O_5$
E_2TTE_2	1.0	$Me_{14}Si_6O_5$
$ET(D'E)(D_2E)$	3.3	$Me_{13}Si_7H_3O_6$
$(EC')_2OE_2$	1.6	$Me_{14}Si_7H_2O_6$
$E_2TD'TE_2$	3.9	$Me_{16}Si_7HO_6$
$(ED'T-)_2$	13.1	$Me_{16}Si_8H_2O_7$
--	3.9	$Me_{17}Si_9H_3O_8$

a) 2.0 M ED'O'E, .01M $L_2(CO)$ClIr in benzene; 60°; 90 hr.; 12% conversion.

b) Structure of products with more than 4 Si-atoms assigned only on basis of assumed mechanism of formation - see text.
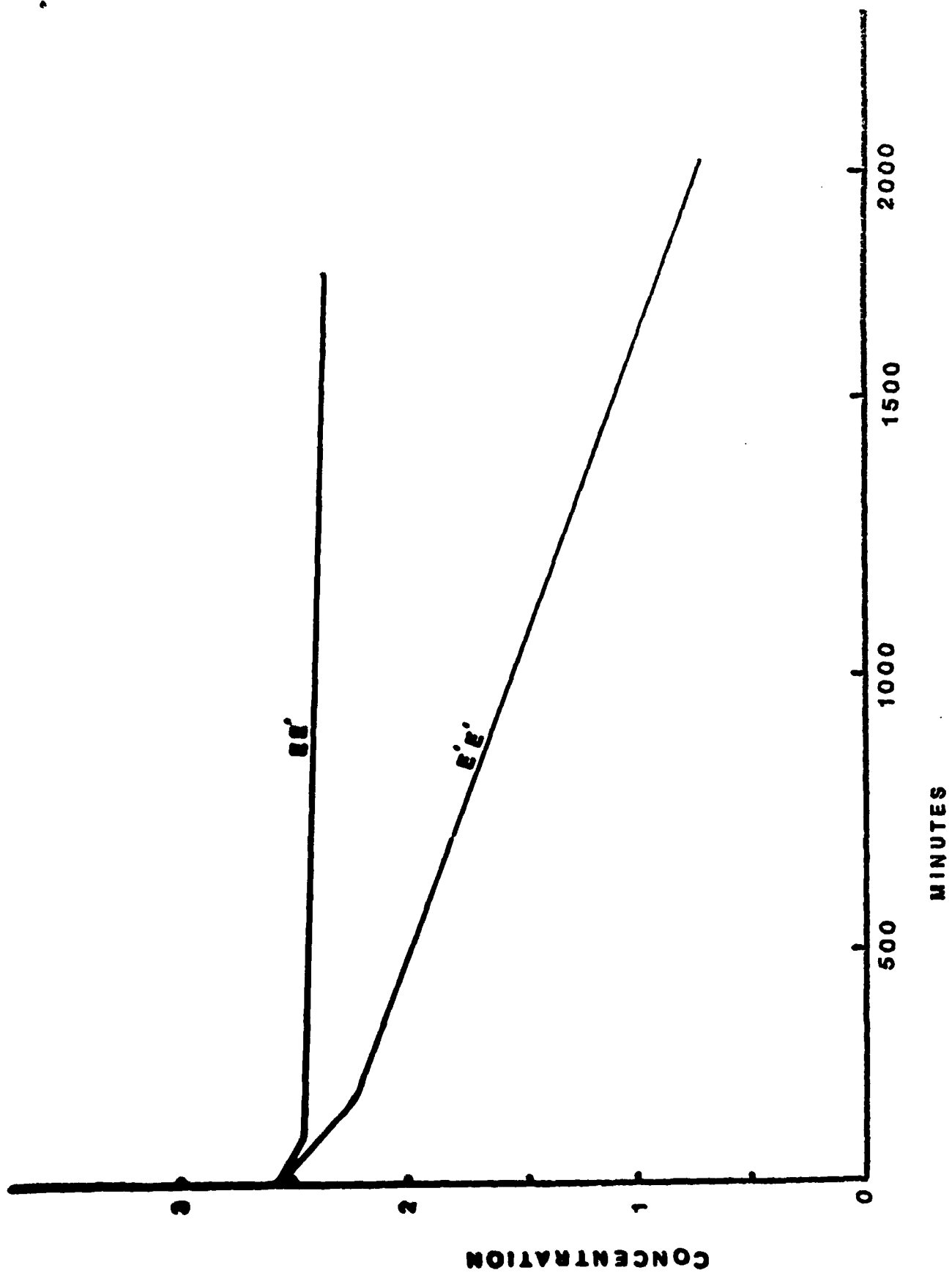
c) GC area % of products only. Minor products (<1 %) omitted.

CAPTIONS TO THE FIGURES

Figure 1.   Concentrations ($M \times 10^3$) of $E'E'$, $E'DE'$ and $E'D_2E'$ vs. time, catalyzed by $2 \times 10^{-3}M$ L$_3$RhCl at 41°.

Figure 2.   Concentrations (moles/ℓ) of EE' and $E'E'$ vs. time, catalyzed by .051M L$_2$(CO)ClIr at 70°.
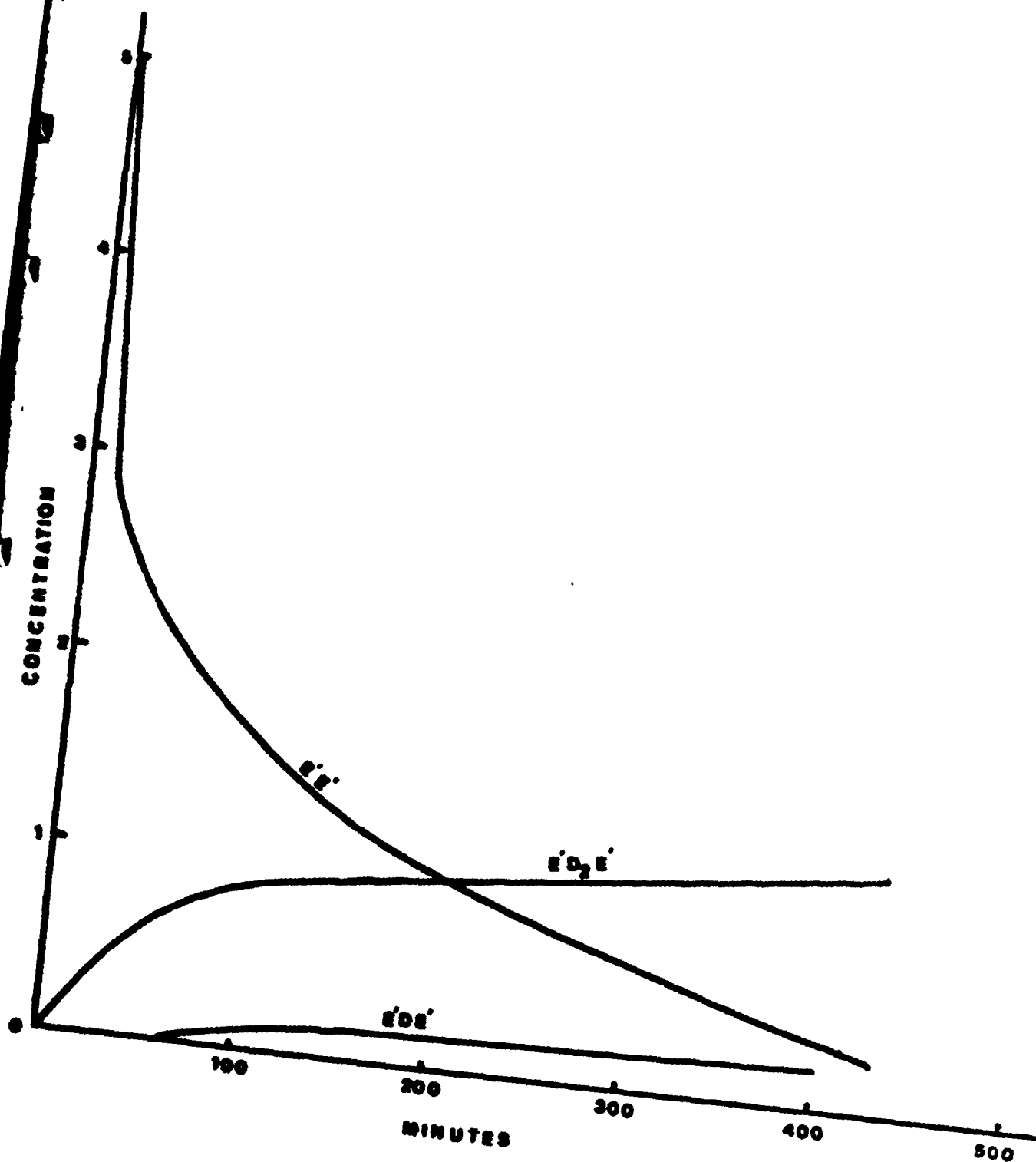
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